Stochastic Diffusion Model for Crystal Size Distribution in an Open Flow System

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The crystal size distribution (CSD) is one of the important characteristics of a continuous crystallizer, which needs to be known for its design and operation. In a crystallizer, for example, a continuous mixed suspension mixed product removal (MSMPR) crystallizer, seed crystals are present in the feed stream and some are formed inside the crystallizer. The growth rates of small crystals may depend on their sizes but they eventually become independent of it as they grow larger (Hartel et al., 1980).

The growth kinetics of a seed crystal in a supersaturated solution is of the first order; solute molecules are transported to the surface of the seed crystal where a cluster of molecules may be integrated (Randolph and Larson, 1971). It has been recognized (Hulbert and Katz, 1964; Randolph and Larson, 1971) that the process of crystal growth is stochastic in nature in that seeds of an equal initial size are known to grow at different rates.

Many researchers have modeled the crystal size distribution using the population balance approach (Randolph and Larson, 1962; Sherwin et al., 1965; Randolph and Larson, 1971; Jančić and Garside, 1975; Randolph, 1978). While the conventional population balance approaches employed by these investigators have stochastic interpretation, it gives rise to a deterministic mathematical model because the resultant population density is only the expected density (Ramkirshna and Borwanker, 1973). Recently, increasing attention has been given to modeling the effect of fluctuations in the crystal growth rate (Lieb, 1973; Randolph and White, 1977; Melikhov and Berliner, 1981). In this work, the Kolmogorov or stochastic diffusion equation is employed as a model for describing the crystal size distribution in a crystallizer or series of crystallizers. The model takes into account: (1) fluctuations in the growth rate, (2) size dependency of the growth rate, and (3) the residence time of the crystal.

MODEL

Consider a continuous flow crystallizer containing the supernatant initially. At any time s ($s > 0$) new seeds appear in the crystallizer from two sources, one is the feed stream and the other nucleation. We assume that the seeds grow independently of one another by attachment of solute molecules in the supernatant maintained at a certain level of supersaturation. Each seed resides in the crystallizer a random length of time before exiting. A further assumption is that the size of a crystal changes continuously during growth. Let $f(x_s,x;t-s)$ be the probability density that a crystal of size x_s at time s will be of size x at time t. It can be shown that $f(x_s,x,t-s)$ satisfies the forward Kolmogorov diffusion equation (Cox and Miller, 1965).

$$\frac{\partial}{\partial t} f(x_s,x;t-s) = \frac{1}{2}\frac{\partial^2}{\partial x^2}[\sigma^2(x) f(x_s,x;t-s)] - \frac{\partial}{\partial x}[\xi(x) f(x_s,x;t\text{-}s)] \tag{1}$$

where the instantaneous variance of the growth rate, $\sigma^2(x)$, and the instantaneous mean of the growth rate, $\xi(x)$, are defined, respectively, as

$$\sigma^2(x) = \lim_{\Delta t \to 0} \frac{\mathrm{Var}[X(t+\Delta t) - X(t) | X(t) = x]}{\Delta t} \tag{2}$$

$$\xi(x) = \lim_{\Delta t \to 0} \frac{E[X(t+\Delta t) - X(t) | X(t) = x]}{\Delta t} \tag{3}$$

If the growth rate is size-independent, $\sigma^2(x)$ and $\xi(x)$ are constants, and consequently, Eq. 1 reduces to

$$\frac{\partial}{\partial t} f(x_s,x;t-s) = \frac{1}{2}\sigma^2 \frac{\partial^2}{\partial x^2} f(x_s,x;t-s) - \xi \frac{\partial}{\partial x} f(x_s,x;t-s) \tag{4}$$

The growth rate may be size-dependent for small crystals, and becomes size-independent for large crystals (Hartel et al., 1980). For this case, it may be assumed that the intensity of growth is a linear (first-order) function of the size of the crystal, x, for the range $a \le x \le b$, and is independent of x for $x > b$, i.e.,

$$\xi(x) = \begin{cases} \lambda^* x, & x \le b \\ \lambda = \lambda^* b, & x > b \end{cases} \tag{5}$$

The natural initial condition for Eq. 1 is

$$f(x_s, x; s-s) = \delta(x_s - x) \tag{6}$$

where $\delta(x_s - x)$ is the dirac-delta function. We may assume that the lower boundary ($x = a$) is a reflecting barrier, signifying that the crystal size will not be smaller than a. The corresponding boundary condition is (Cox and Miller, 1965)

$$\left. \frac{1}{2}\frac{\partial}{\partial x}[\sigma^2(x) f(x_s, x; t-s)] - \xi(x) f(x_s, x; t-s) \right|_{x=a} = 0 \tag{7}$$

The upper boundary may be assumed to be natural, that is, $f(x_s, x; t-s)$ is finite as $x \to \infty$. This is reasonable if a crystal can grow to a sufficiently large size.

An analytical solution to Eq. 4 for the size-independent growth process, subject to the initial and boundary conditions given in the preceding paragraph, may be obtained by the method of images (Sommerfeld, 1949; Cox and Miller, 1965). This gives

$$\begin{aligned} f(x_s,x;t-s) &= \frac{1}{\sigma\sqrt{2\pi(t-s)}}\left\{\exp\left[-\frac{(x - x_s - \xi(t-s))^2}{2\sigma^2(t-s)}\right]\right. \\ &\quad \left. + \exp\left[-\frac{4\xi(x_s - a)(t-s) + (x + x_s - 2a - \xi(t-s))^2}{2\sigma^2(t-s)}\right]\right\} \\ &\quad - \frac{2\xi}{\sigma^2}\exp\left[\frac{2\xi(x-a)}{\sigma^2}\right][1 - Z(\gamma)] \end{aligned} \tag{8}$$

where $Z(\gamma)$ is the standard normal distribution, and

$$\gamma = \frac{[x + x_s - 2a + \xi(t-s)]}{\sigma\sqrt{(t-s)}}$$

In general, it is difficult to solve analytically Eq. 1 with variable coefficients; however, it can be done numerically.

A crystal grows in a crystallizer until it exits. Let T be the residence time of the crystal in the crystallizer and $E(\tau)$ the residence time distribution of T. The probability that the crystal does not exit in the time interval (s,t) is

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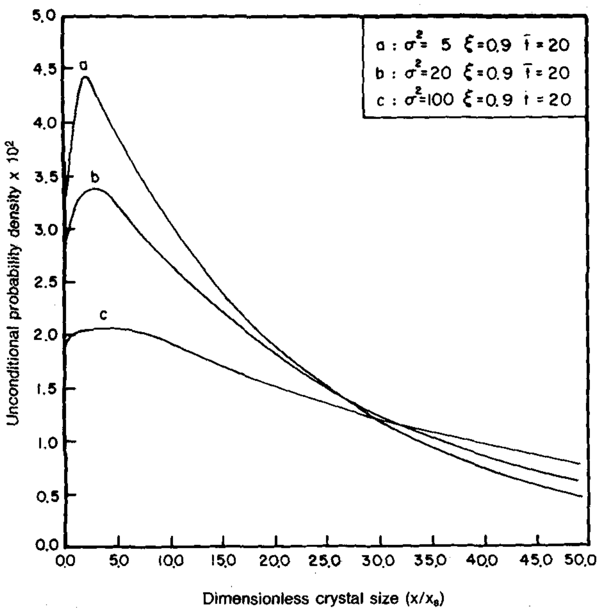

Figure 1. Crystal size distribution obtained from Eq. 12, corresponding to different instantaneous variances of the growth rate, σ^2.

$$Pr[T > (t-s)] = \int_{(t-s)}^{\infty} E(\tau)d\tau = 1 - \int_{0}^{(t-s)} E(\tau)d\tau \quad (9)$$

For an MSMPR crystallizer, the residence time distribution is expressed as

$$\mathrm{E}(\tau) = \frac{1}{\bar{t}}\exp(-\tau/\bar{t}) \quad (10)$$

where $\bar{t}$ is the mean residence time of the crystal in the crystallizer. If a system containing n completely mixed crystallizers of equal size connected in series without backflow is employed, $E(\tau)$ in Eq. 9 is replaced by (Froment and Bischoff, 1979)

$$E(\tau) = \frac{1}{(n-1)!\bar{t}}\left(\frac{\tau}{\bar{t}}\right)^{n-1}\exp(-\tau/\bar{t}) \quad (11)$$

For an arbitrary flow crystallizer, the residence time distribution can be determined as in Fan. et al. (1982).

The transition probability density function $f(x_s,x;t-s)$ is conditional on the crystal not exiting until time t. The unconditional probability density at time t is obtained as

$$\int_0^t f(x_s,x;t-s)Pr[T \geq (t-s)]ds \Big/ \int_0^t Pr[T \geq (t-s)]ds \quad (12)$$

where $Pr[T > (t-s)]$ is given in Eq. 9. So far we have considered the case where all seeds at initial time $s (s > 0)$ have the same size x_s. If seeds in the feed stream are not uniform in size and/or if nucleation occurs in the crystallizer, Eq. 12 must be modified by taking into account the initial size distribution as elaborated below.

Consider a continuous flow crystallizer containing the supernatant initially. Let $m(s)$ denote the rate of seeds entering the crystallizer with the feed stream and $n(s)$ be the rate of seed formation by nucleation in the crystallizer. The initial size distributions for $m(s)$ and $n(s)$ are denoted by $g(x_s)$ and $h(x_s)$, respectively. The probability density function of the crystal size in the crystallizer at any time t can then be expressed as

$$\frac{\int_0^t \int_{x_s} [m(s)g(x_s) + n(s)h(x_s)]f(x_s,x;t-s)dx_s Pr[T > (t-s)]ds}{\int_0^t [m(s) + n(s)]Pr[T > (t-s)]ds} \quad (13)$$

DISCUSSION

The present continuous model rests on the knowledge of the instantaneous mean, $\xi(x)$, and the instantaneous variance, $\sigma^2(x)$, of crystal growth rate for a given crystallization process. These parameters may be estimated and related to the crystal size. Suppose that we start initially with seeds of equal size x_i. After an arbitrary but short time interval, the process may be stopped, and the resultant crystal size distribution can be measured by means of an image analyzer. From the mean and variance of this distribution we can obtain estimates of the instantaneous mean, $\xi(x_i)$, and the instantaneous variance, $\sigma^2(x_i)$, and eventually establish a correlation between each estimate and the crystal size, x. Needless to say, other approaches may be developed for estimating these two variables.

It is expected that an increase in the instantaneous variance of the growth rate in a crystallization process would increase the variance or dispersion of the crystal size distribution. To demonstrate the effect of a large instantaneous variance on their dispersions, the CSD's have been generated for the following three conditions based on the present continuous model:

a. $\sigma^2 = 5, \xi = 0.9, \bar{t} = 20$
b. $\sigma^2 = 20, \xi = 0.9, \bar{t} = 20$
c. $\sigma^2 = 100, \xi = 0.9, \bar{t} = 20$

The steady state results ($t \rightarrow \infty$) in Figure 1 show that an increase in the instantaneous variance, σ^2, results in an appreciable increase in the dispersion of the CSD, as expected.

In the examples given above, we have assumed that all seeds have an equal initial size. If the seeds in the field stream are not uniform or if nucleation occurs in the crystallizer, we have the initial size distributions of seeds (Garside et al., 1979). For this case the crystal size distribution can be obtained from Eq. 13.

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NOTATION

a = lower bound of the crystal size
b = crystal size above which the growth rate becomes independent of the size
$E[\ ]$ = expected value of the given random variable
$E(\tau)$ = exit age distribution or density function of the residence time
$f(x_s,x;t-s)$ = probability density function that a crystal of size x_s at time s will be of size x at time t
$h(x_s)$ = initial size distribution of seeds formed in the crystallizer by nucleation
$h(x_s)$ = initial size distribution of seeds entering the crystallizer
$m(s)$ = feed rate of seeds
$n(s)$ = rate of seed formation in the crystallizer by nucleation
T = residence time of a crystal in the crystallizer
$\bar{t}$ = mean residence time of crystals in the crystallizer
Var[ ] = variance of the given random variable
x_s = initial size of seeds
$Z(\gamma)$ = standard normal distribution

Greek Letters

$\xi(x)$ = instantaneous mean of crystal growth rate
$\sigma^2(x)$ = instantaneous variance of crystal growth rate

LITERATURE CITED

Cox, D. R., and H. D. Miller, *The Theory of Stochastic Processes*, John Wiley,New York (1965).

Fan, L. T., J. R. Too and R. Nassar, "Stochastic Flow Reactor Modeling: A General Continuous Time Compartmental Model With First-Order Reactions," *Residence Time Distribution Theory In Chemical Engineering*, edited by Pethö and R. D. Noble, Verlag Chemie Gmbh., D-6940, Weinheim (1982).

Froment, G. F., and K. B. Bischoff, *Chemical Reactor Analysis and Design*, John Wiley, New York (1979).

Garside, J., I. T. Rusli, and M. A. Larson, "Origin and Size Distribution of Secondary Nuclei," *AIChE J.*, **25**, 57 (1979).

Hartel, R. W., et al., "Crystal Kinetics for Sucrose-Water System," *AIChE Sym. Ser.*, **76**, (193), 65 (1980).

Hulburt, H. M., and S. Katz, "Some Problems in Particle Technology," *Chem. Eng. Sci.*, **19**, 555 (1964).

Jančić, S., and J. Garside, "On the Determination of Crystallization Kinetics from Crystal Size Distribution Data," *Chem. Eng. Sci.*, **30**, 1299 (1975).

Lieb, E. B., "Perfect-Mixing Approximation of Imperfectly Mixed Continuous Crystallizers," *AIChE J.*, **19**, 646 (1973).

Melikhov, I. V., and L. B. Berliner, "Simulation of Batch Crystallization," *Chem. Eng. Sci.*, **36**, 1021 (1981).

Ramkrishna, D., and J. D. Borwanker, "A Puristic Analysis of Population Balance-I," *Chem. Eng. Sci.*, **28**, 1423 (1973).

Randolph, A. D., "A Perspective on Population Models for Crystal-size Distribution," 7th Symp. of Ind. Crystalliz., Warsaw, Poland (Sept. 25–27, 1978).

Randolph, A. D., and M. A. Larson, "Transient and Steady State Size Distributions in Continuous Mixed Suspension Crystallizers," *AIChE J.*, **8**, 639 (1962).

Randolph, A. D., and M. A. Larson, *Theory of Particulate Processes*, Academic Press, New York (1971).

Randolph, A. D., and E. T. White, "Modeling Size Dispersion in Prediction of Crystal-size Distribution," *Chem Eng. Sci.*, **32**, 1067 (1977).

Sherwin, M. B., R. Shinnar, and S. Katz, "Dynamic Behavior of the Well-Mixed Isothermal Crystallizer," *AIChE J.*, 13, 1141 (1967).

Sommerfeld, A., *Partial Differential Equations in Physics*, Academic Press, New York (1949).

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Collocation Solution of Creeping Newtonian Flow through Sinusoidal Tubes: a Correction

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Periodically constricted tubes have frequently been used in modeling flow through porous media (Payatakes et al., 1973a,b,c; 1974a,b; Slattery, 1974; Sheffield and Metzner, 1976; Payatakes and Neira, 1977; Fedkiw and Newman, 1977; Neira and Payatakes, 1978, 1979; Deiber and Schowalter, 1979, 1981; Oh and Slattery, 1979; Tien and Payatakes, 1979; Payatakes et al., 1980; Giordano and Slattery, 1982). Laminar flow through tubes with variable radius has also been studied in connection with other applications (Dodson et al., 1971; Chow and Soda, 1972, 1973a,b; Lessen and Huang, 1976).

Payatakes et al. (1973b) used a finite difference method to solve the full Navier-Stokes equations for flow through a periodically constricted tube. Thus, their solution remains valid when the nonlinear inertial terms become important (which is the case for Reynolds number greater than roughly 1 to 30). In many cases of practical interest, including oil flow through porous reservoir rock, inertial effects may be neglected. Neira and Payatakes (1979) used a collocation method to solve Stokes' equation for creeping flow in a sinusoidal tube. A desirable feature of the collocation method is the analytical form of the approximate solution. Unlike the finite difference method, no interpolation is required to compute quantities at off-node positions, and the collocation solution is well suited to analytical manipulation.

Regrettably, the collocation solution of Neira and Payatakes (1979) is unsatisfactory because it gives a velocity singularity along the tube axis. This paper presents a modification of their solution that rectifies this problem.

Figure 1 depicts a segment of a tube with wall radius varying sinusoidally with axial position. The tube has minimum radius r_1, maximum radius r_2, and wavelength h. Mean radii and reduced amplitudes are defined by $r_a = (r_1 + r_2)/2$ and $b = (r_2 - r_1)/(r_2 + r_1)$, respectively. It is convenient to introduce dimensionless variables as follows:

$$r^* = r/h,\ r_1^* = r_1/h,\ r_2^* = r_2/h,\ r_a^* = r_a/h,\ z^* = z/h,\ r_w^* = r_w/h \tag{1}$$

The dimensionless wall radius is given by:

$$r_w^* = r_a^*[1 + b\sin 2\pi(z^* - 1/4)] \tag{2}$$

The tube constriction or point of minimum radius occurs at the origin of the z-axis. The average velocity at this cross section is denoted by v_o. This velocity is used to form dimensionless velocity components:

$$v_r^* = \frac{v_r}{v_o}, \quad v_z^* = \frac{v_z}{v_o} \tag{3}$$

A dimensionless stream function is defined as follows:

$$v_r^* = \frac{1}{r^*}\frac{\partial\psi^*}{\partial z^*}, \quad v_z^* = -\frac{1}{r^*}\frac{\partial\psi^*}{\partial r^*} \tag{4}$$

Stokes' equation for creeping flow may be expressed in terms of the stream function as

$$E^{*4}\psi^* = 0 \tag{5}$$

where

$$E^{*2} \equiv \frac{\partial^2}{\partial r^{*2}} - \frac{1}{r^*}\frac{\partial}{\partial r^*} + \frac{\partial^2}{\partial z^{*2}} \tag{6}$$

Equation 5 must be solved subject to the following boundary conditions:

1. No slip at the tube wall.

$$\frac{\partial\psi^*}{\partial r^*} = \frac{\partial\psi^*}{\partial z^*} = 0 \text{ at } r^* = r_w^*(z^*) \tag{7}$$

Equation 7 requires ψ^* = constant along the wall. For conve-

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